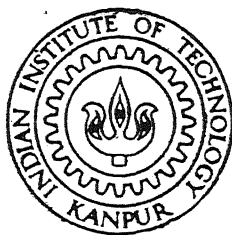


MODELLING AND SIMULATION OF SULPHUR DIOXIDE REMOVAL IN A PACKED BED REACTOR WITH ACTIVE SODIUM BICARBONATE

A Thesis Submitted
in Partial Fulfillment of the Requirements
for the Degree of
Master of Technology

by
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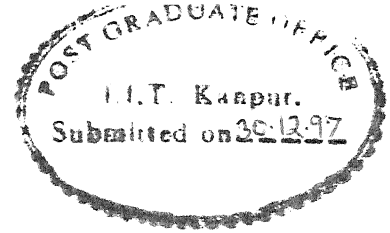
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CERTIFICATE



It is certified that the work contained in thesis titled 'MODELLING AND SIMULATION OF SULPHUR DIOXIDE REMOVAL IN A PACKED BED REACTOR WITH ACTIVE SODIUM CARBONATE', by ROHIT JOSHI, has been carried out under my supervision and this work has not been submitted elsewhere for a degree.


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ABSTRACT

A packed bed reactor model for the sulphation of active sodium carbonate has been developed to simulate sulphur dioxide breakthrough curves. Breakthrough curves obtained from the formulated model were then validated by comparing them with those available in literature. Kinetic data and other physical parameters available in the literature were used to predict the breakthrough curves for the above mentioned system using the formulated model. Simulated breakthrough curves corroborated fairly well with the experimental results reported in the literature.

*Dedicated
To
My Grandparents*

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NOMENCLATURE

A	Reactant gas (SO ₂)
A _g	Surface area of grains of solid. cm ² /sec
A _p	Area of a particle. cm ²
B,D	Solid reactant and product respectively
b,c,d	Stoichiometric coefficients
C _A	Molar concentration of SO ₂ at the outlet. g.moles/cm ³
C _{A0}	Molar concentration of SO ₂ at the inlet. g.moles/cm ³
D _e	Effective diffusivity, cm ² /sec
D _e (0)	Initial effective diffusivity, cm ² /sec
D _e (X)	Effective diffusivity at conversion x. cm ² /sec
F _p ,f _p	Shape factor for grains of solid
F _g ,f _g	Shape factor for particle
k	Intrinsic reaction rate, cm/sec
r _c	Grain radius, cm
r ₀	Initial radius of grain. cm
t	time of reaction
t [*] ,T [*]	dimensionless reaction time
T	tempreture, K
U	superficial velocity, cm/sec
V _g	Volume of grains of solid reactant, cm ³ /gm
V _p	Pore volume of the particle, cm ³
w	Fractional volume of reactive solids
x,X	Fractional conversion of solid
y	Distance along the flow, cm
y [*]	Dimensionless distance

Greek Symbols

α	A distributed parameter
β	A function of x and σ
γ	Grain size change factor
ϵ_p	Porosity of a particle
ϵ_x	Porosity at x
ϵ_0	Initial porosity
ϵ_t	Bed porosity
ξ	Ratio of r_c and r_0
σ	Characteristic reaction modulus
ρ_B	Molar density of solid reactant
ψ	Dimensionless concentration

1. INTRODUCTION

The increased presence of sulphur dioxide in the atmosphere causes several adverse effects on human health, vegetation, material and visibility. Excessive emissions of sulphurdioxide lead to acidification of rain water, lakes and soils. The various methods for control of sulphur dioxide emission include burning less sulphur fuels, removing sulphur from fuel, substitution of another energy source, cleaning up of the flue gas for removal of sulphur dioxide as far as possible right at source and eventual dispersion through stacks.

Among various control methods, cleaning up of flue gases received maximum attention in recent years. The increased interest in dry flue gas desulphurisation processes has led to the need for evaluating various sorbents which remove sulphur dioxide by chemical reaction, adsorption, catalytic reaction or a combination of processes. Sulphur dioxide removal by porous solid reactants was found to be limited by one or more of the following steps: Bulk diffusion of sulphur dioxide to the particle, diffusion of sulphur dioxide through pores, diffusion of sulphur dioxide through product layer, filling up of small pores causing decrease in reactive area, built up of product layer at entrance of pores causing pore closure, less surface area due to sintering and reduced kinetic reaction rates at low temperatures.

Evaluation of sorbents under various process conditions may be facilitated if their performance can be predicted theoretically, using an appropriate model. In the present study an attempt has been made to formulate a mathematical model to predict breakthrough curves for flue gas desulphurisation under dry condition in a packed bed reactor using active sodium carbonate as a sorbent. Before modelling an existing physical system, it is essential to examine it and then decide parameters which can be used to form

mathematical expression representing the physical problem. Breakthrough curves obtained from the formulated model can then be validated by comparing them with the actual results obtained from the physical system which was modelled. Once the simulated breakthrough curves are validated they can be used to predict the performance of suitable sorbents in a packed bed reactor under similar conditions. The same can then be used to design packed bed reactors for the removal of sulphur dioxide using suitable sorbents.

2. BACKGROUND INFORMATION

2.1 Sulphur Dioxide Control Technologies

There are four possible approaches that may be used individually or in combination to control sulphur dioxide emission from fossil fuel combustion. They include fuel switching, fuel cleaning and fuel conversion, desulphurisation of flue gases, dispersion from tall stacks. Several combustion power facilities around the world have switched over to low sulphur fuels which is found to be fastest and easiest means of complying with sulphur dioxide emission regulations. Sulphur removal from fuels before combustion represents a more likely alternative if technology for removing sulphur from fuels is available for economic implementation. Sulphur is present in coal in varying amount in pyritic and organic forms. Tall stacks are obvious means of reducing ambient ground level concentration of sulphur dioxide at cost significantly less than those for flue gas scrubbing but total amount of emission remains the same which may adversely affect the environment in many ways.

An optimal combination of flue gas desulphurisation for the control of sulphur dioxide at source and subsequent dispersion with the help of suitable stack might be described as the approach for achieving pollution reduction relatively independent of uncertainties of meteorology and fuel quality. Flue gas desulphurisation is presently the most commonly used technology to comply with sulphur dioxide emission requirements. In fact, dry flue gas desulphurisation will be a promising technology compared to conventional wet scrubbing in view of the requirement of dispersion as stated above.

The flue gas desulphurisation may be grouped according to two classifications

1. Throw away or regenerative
2. Dry or wet

Throw away process is that in which waste product is discarded, as a result fresh chemical must be continually added. In regenerative process as the name implies, the chemistry is such that the removal agent can be continually regenerated in closed loop system. Wet or dry processes are differentiated simply by whether the product formed is dry or wet. The removal system typically involves the use of adsorption, absorption or catalytic processes.

Dry desulphurisation of flue gases may be achieved by passing flue gas through the packed bed containing reactive sorbent dispersed in an inert media. Desulphurisation takes place due to reaction of sorbent with sulphur dioxide, knowledge of gas-solid reaction is thus essential in order to understand the phenomena of sulphur dioxide removal using reactive sorbents.

2.2 Elements of Gas Solid Reaction Systems Involving Single Particle

The smallest representative unit of gas-solid reaction system is the interaction of single particle with a moving gas stream. Let us consider a gas-solid reaction of the type



Where b, c and d are the stoichiometric coefficients. Over all reaction process may involve the following individual steps:

1. Gas phase mass transfer of the gaseous reactant from the bulk of the gas stream to the external surface of solid particle.
2. Diffusion of gaseous reactant through the pores of the solid matrix, which could consist of a mixture of solid reactants and products.
3. Adsorption of the gaseous reactant on the surface of solid matrix.
4. Desorption of the gaseous product from the surface of solid matrix.
5. Diffusion of gaseous reactant product through the pores of solid matrix.

6. Gas phase mass transfer of the gaseous product from the external surface of the solid to the bulk of the gas stream.

Heat transfer:

For exothermic or endothermic reactions the diffusional and reaction steps will be accompanied by

1. Convective (and possibly radiative) heat transfer between the gas stream and surface of solid particle, and
2. Conduction heat transfer within the solid reactant-product matrix.

Structural changes:

The reaction and heat transfer processes could lead to structural changes. such as sintering or changes in pore structure. which in turn could have a marked effect on the over all reaction rate.

2.3 Grain Model

In many gas-solid reactions encountered in chemical and metallurgical processes. solid products are formed. Such reactions may be described by the general equation



The overall volume of solid may increase or decrease depending on the relative density of solid product compared with that of solid reactant. In most cases however the change is rather small so that the overall size may be regarded constant.

When solid reactant is non porous there is a sharp boundary between the reacted and unreacted core. In general case of porous solid there is a gradual change in the degree of conversion throughout the particle. The external layer will be completely reacted after a certain time. and the thickness of completely reacted layer will increase towards the

interior of the particle. Under these conditions in contrast to non porous solids the reaction within the partially reacted zone occurs simultaneously with diffusion of fluid in this zone.

When chemical reaction presents the major resistance to the overall progress of reaction, the concentration of fluid reactant will be constant everywhere and the reaction will occur uniformly throughout the volume of the solid. If on the other hand, pore diffusion presents the major resistance, the reaction will occur in narrow boundary between the unreacted and completely reacted zones. In the intermediate region where the resistances presented by chemical reaction and pore diffusion are of comparable magnitude, both processes must be considered simultaneously.

2.3.1 Assumptions Made in the Formulation of Grain Model

A particle is usually made up of fine grains with or without some binding agents. The overall shape may be approximated by that of a slab, a long cylinder or a flat plate, made up of individual grains of equal size, which could again be spheres, long cylinders or flat plates. In considering such a particle to be made up of large number of discrete grains, we are not far from the truth, although in general the assumptions of uniform size of grain and its regular shape are not accurate.

The assumptions made in the formulation of grain model are discussed by Shon and Szekely (1972) and will be merely listed here.

1. The pseudosteady state approximation is appropriate for describing the concentration of reactant within the particle.
2. The resistance due to external mass transfer is negligible.
3. Diffusion within the particle is either equimolar counterdiffusion or is at low concentration of diffusing species, and the effective diffusivities of gaseous reactant and product are equal and uniform throughout the particle.

4. The system is isothermal.
5. The solid structure is macroscopically uniform and unchanged by reaction.
6. Diffusion of the gaseous reactants through the product layer of individual grain is not rate limiting.
7. Viscous flow contribution to the mass transfer within the particle is negligible.

2.3.2 Chemical Reaction Controlled Model

Chemical kinetics control the process when the rate of diffusion through the interstices among the grain presents the negligible resistance to the progress of reaction. The concentration of gaseous reactant is uniform throughout the solid. The grains are assumed as non porous and within each grain the reaction front retains its original geometric shape as reaction proceeds. When the product layer has any degree of porosity, for the n^{th} order reaction it can be written as (Shon and Szekely, 1972).

$$T^* = (1 - (1 - X)^{1/f_g}) \quad 2.3$$

Where T^* , X , f_g are dimensionless time, fractional conversion and grain shape factor respectively. The grain shape factor has value of 1, 2 and 3 for flat plates, long cylinders and spheres respectively.

2.3.3 Reaction Controlled by Diffusion through the Product Layer

In case of pore diffusion being rate limiting step, reaction occurs in a narrow zone separating the unreacted core and completely reacted layer, where the reactant concentration becomes very small. Under this situation it can be written as (Shon and Szekely, 1972)

$$T^* = \sigma^2 A(X) \quad 2.4$$

Where,

$$A(X) = X^2 \quad \text{For } f_p = 1 \quad 2.5$$

$$= X + (1 - X) \ln(1 - X) \quad \text{For } f_p = 2 \quad 2.6$$

$$= (1 - 3(1 - X)^{2/3} + 2(1 - X)) \quad \text{For } f_p = 3 \quad 2.7$$

and σ is the reaction modulus

2.3.4 Reaction Controlled by Simultaneously Chemical Reaction and Pore Diffusion

When chemical reaction and pore diffusion control the overall rate of reaction then approximate relationship has been proposed by Shon and Szekely (1972).

$$T^* = (1 - (1 - X)^{1/f_g} + \sigma^2 A(X)) \quad 2.8$$

Where σ is a characteristic parameter called reaction modulus. Its value is given as

$$\sigma = \frac{V_p}{A_p} \left[\frac{(1 - \epsilon_0)}{2D_e} \frac{A_g}{V_g f_g} f_p \right]^2 \quad 2.9$$

An estimation of reaction modulus provides information as to one needs data on chemical kinetics or pore diffusion or both, in order to predict the relationship between conversion and time. If σ is much smaller than unity, one needs kinetic parameter only, if it is much larger than unity, then only diffusion parameter is required. If σ is around unity, both kinetic and diffusion parameters are required.

2.3.5 Diffusion Controlled Model with Changing Porosity

In some system, the reaction of porous solid with a gaseous reactant often seriously affects the macroporosity of particles due to shrinking or swelling due to density differences of solid reactant and product. Accounting this swelling or shrinking by a

characteristic factor γ (Ramachandran and Smith, 1977) the pore diffusion model can be modified as

$$T^* = \sigma_x^2 A(X) \quad 2.10$$

Where σ_x has been presented for varying diffusivity. $D_e(x)$, which can be given as (Ghosh, 1987);

$$D_e(x) = D_e(o) \left(\frac{\epsilon_x}{\epsilon_0} \right)^2 \quad 2.11$$

Where $D_e(o)$ is the original diffusivity and ϵ_x is given as

$$\epsilon_x = 1 - (1 - \epsilon_0) [\gamma - (1 - \gamma)(1 - X)] \quad 2.12$$

and

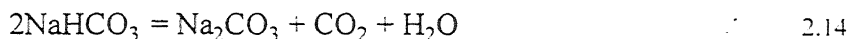
$$\gamma = \frac{d\rho_B}{b\rho_d} (1 - \epsilon_p) \quad 2.13$$

Where b and d are the stoichiometric coefficients and ρ_B and ρ_d are the molar densities of solid reactant and product. If γ is greater than 1 swelling takes place and if less than 1 shrinkage develops.

2.4 Kinetics of Sulphation of Active Sodium Carbonate

The active sodium carbonate is obtained by thermally decomposing pure sodium carbonate, the reactant becomes highly porous. Erdos et al. (1989) reported that active sodium carbonate prepared by thermal decomposition of sodium carbonate is more reactive than anhydrous sodium carbonate prepared by dehydration of hydrated carbonates.

Thermal decomposition of sodium bicarbonate above 115°C is reasonably fast at atmospheric pressure yielding chemically anhydrous sodium carbonate according to the equation

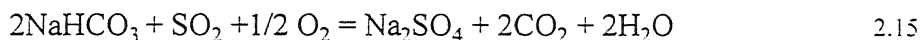


$$F_f = 6.79 \text{ K Cal}$$

The temperature at which decomposition occurs will depend on the partial pressure of carbon dioxide and water vapour present, which is well below equilibrium values at stack gas conditions. The sodium carbonate formed is known to have high surface area. The temperature at which sodium bicarbonate decomposes has been shown to influence the reactivity of sodium carbonate with sulphur dioxide (Erdos et. al.).

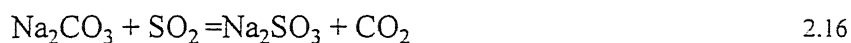
2.4.1 Reaction with Sulphur Dioxide

The overall reaction of sodium bicarbonate with sulphur dioxide has following form



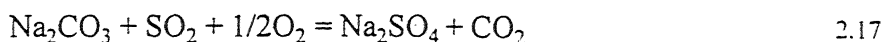
$$F_f = -69.66 \text{ K Cal}$$

This is generally accepted reaction scheme. It assumes that reaction is followed by the reaction between active sodium carbonate and sulphur dioxide. The active sodium carbonate reacts readily with sulphur dioxide yielding sodium sulphite as follows



$$F_f = -13.00 \text{ K Cal}$$

and in the presence of oxygen it reacts with sulphur dioxide yielding sodium sulphate according to the reaction



$$F_f = -76.45 \text{ K Cal}$$

Since the active sodium carbonate was obtained by thermally decomposing pure sodium bicarbonate, the reactant becomes highly porous. For porous solid reactant, gas-solid reaction models based on grain structure of solid have been reported to be appropriate (Ghosh and Maiti, 1989).

For conditions typical of the experiments for sulphation of active sodium carbonate, predicted reaction time, t , for complete conversion was calculated to be 85 seconds for pellet of 12.7 mm diameter using film diffusion model by Bhaskar, 1994. This predicted time was much less than the actual time required for same conversion as observed by Bhaskar, 1994, thus confirming little contribution by gas film diffusion for the overall rate.

2.4.2 Effect of Temperature on Sulphation

In general sulphation of active sodium carbonate at high temperature is preferred due to increased reaction rate at high temperatures. Increase in conversion due to increase in temperature from 250°C to 300°C is negligible (Bhaskar, 1994). This may be due to sintering effects of active sodium carbonate which offsets the increased reaction rate in that range

2.4.3 Structural Examination of Active Sodium Carbonate

The scanning electron micrograph of active sodium carbonate prepared by decomposition at temperature 150°C, 250°C and 350°C showed the formation of gas holes due to evolution of carbon dioxide and water vapour (Bhaskar, 1994). The particles of active sodium carbonate were smaller when decomposed at 150°C whereas they were relatively

larger when decomposed at 250°C , whereas at 350°C active sodium carbonate lost both its grain structure as well as gas holes as observed by Bhaskar, 1994. This may be due to sintering that might have occurred at high temperature.

When active sodium carbonate is allowed to react with sulphur dioxide it was observed by Bhaskar, 1994 that at temperature of 250°C growth of sulphated layer occurred as well as there was a decrease in size of particles and gas holes. The decreased size of pores may have contributed to pore diffusion controlling the progress of reaction.

The existence of straight line relationship according to chemical reaction model does not necessarily mean that the progress is controlled by chemical reaction, because this straight line is very difficult to distinguish from the curve for pore diffusion in many cases. This leads to an incorrect assumption of chemical reaction control, whereas the reaction is controlled by ash layer diffusion or was a mixed control.

Sulphur mapping was uniformly dense throughout the area of pellet for radial position. It was less dense towards the core of the pellet also a definite interface in the concentration of sulphur was observed (Bhaskar, 1994). This means that the sulphation reaction is uniform and complete on the outer surface of the pellet and there was a narrow zone in which sulphur concentration drops to a small value. This supports the hypothesis that reaction is chemically controlled for some initial time during which the reaction is uniform throughout the particle leading to partial reaction of inner core. As the reaction proceeds, the the formation of sulphate decreases the pore diffusion which leads to the formation of separate zones of completely reacted and partially reacted portion radially inwards the particle.

3. SCOPE OF THE WORK

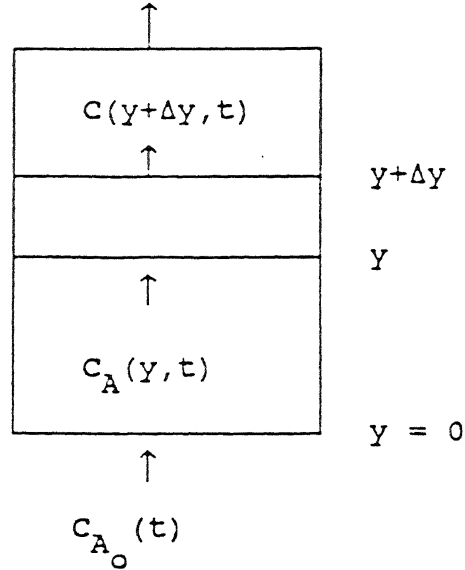
While going for modelling it is essential to examine the physical problem, which is to be modelled. Physical problem is then replaced by equivalent mathematical expression. Once the mathematical expression representing the physical problem is formulated, it can be solved by suitable technique. Results obtained from the mathematical model are then compared with the actual results of the physical problem.

In the present study attempt has been made to

1. Formulate a fixed bed reactor model for the sulphation of active sodium carbonate (freshly prepared by heating sodium bicarbonate in the reactor) dispersed in sand.
2. Simulate breakthrough curves for the above mentioned system using the formulated model.
3. Validate the simulated curves by comparing them with the experimental results available in the literature.

4. PACKED BED REACTOR MODELLING

Let us assume a fixed bed reactor filled with reactive porous solid. Pollutant gas is introduced from the bottom of the reactor.



An elemental volume in the reactor is assumed whose thickness is Δy and cross sectional area is S . The pollutant gas is introduced in the reactor with a superficial velocity of U and is assumed to react with spherical porous reactive solid whose porosity is ϵ_p according to the grain model. The porous reactive solid is dispersed in a bed of porosity ϵ_v . The fractional volume of the reactive solid of density ρ_B in the reactor is w and the fractional conversion of the sorbent which varies with reaction time is given as x . then the material balance can be written as follows

$$(UC_A S)_{y,t} - (UC_A S)_{y+\Delta y,t} = \frac{\delta}{\delta t} \left[(\epsilon_p + \epsilon_v) \Delta y C_A S + \frac{\partial y S \rho_B w x}{b} (1 - \epsilon_p)(1 - \epsilon_v) \right] \quad 4.1$$

Assuming $U, \epsilon_p, \epsilon_v, S$ are constant, taking the limit $\delta t \rightarrow 0$ and rearranging the continuity equation takes the form

$$U \frac{\delta C_A}{\delta y} + (\epsilon_p + \epsilon_v) \frac{\delta C_A}{\delta t} + \frac{(1 - \epsilon_p)}{b} (1 - \epsilon_v) w \rho_B \frac{\delta x}{\delta t} = 0 \quad 4.2$$

According to the grain model, each of a particle is reacting according to unreacted shrinking core model. The continuity equation given above may be expressed in terms of dimensionless parameters explained as follows containing the characteristic features of grain model.

$$\psi = \frac{C_A}{C_{A0}}, \quad t^* = \left(\frac{bkC_{A0}A_g}{\rho_B F_g V_g} \right) t \quad \text{and} \quad 4.3$$

$$y^* = \frac{k}{U} w \left(\frac{A_g}{V_g F_g} \right) (1 - \epsilon_p)(1 - \epsilon_v) y \quad 4.4$$

writing the partial derivatives in terms of dimensionless variables, we have

$$\frac{\delta C_A}{\delta y} = \frac{\delta \psi}{\delta y^*} C_{A0} \frac{k}{U} w \left(\frac{A_g}{F_g V_g} \right) (1 - \epsilon_p)(1 - \epsilon_v) \quad 4.5$$

$$\frac{\delta C_A}{\delta t} = \frac{\delta \psi}{\delta t^*} \left(\frac{bkC_{A0}A_g}{\rho_B F_g V_g} \right) C_{A0} \quad 4.6$$

$$\frac{\delta x}{\delta t} = \frac{\delta x}{\delta t^*} \left(\frac{bkC_{A0}A_g}{\rho_B F_g V_g} \right) \quad 4.7$$

Substituting the derivatives into the continuity equation, final form may be obtained as follows

$$\begin{aligned}
 UC_{.40} \frac{k}{U} w \left(\frac{A_g}{F_g V_g} \right) (1 - \epsilon_p)(1 - \epsilon_v) \frac{\delta \psi}{\delta y^*} + (\epsilon_p + \epsilon_v) \left(\frac{bkC_{.40}A_g}{\rho_B F_g V_g} \right) C_{.40} \left(\frac{\delta \psi}{\delta t^*} \right) + \\
 \frac{(1 - \epsilon_p)(1 - \epsilon_v)}{b} w \left(\frac{bkC_{.40}A_g}{\rho_B F_g V_g} \right) \rho_B \frac{\delta x}{\delta t^*} = 0
 \end{aligned} \quad 4.8$$

Eliminating the common term and rearranging the continuity equation we get

$$\frac{\delta \psi}{\delta y^*} + \alpha \frac{\delta \psi}{\delta t^*} + \frac{\delta x}{\delta t^*} = 0 \quad 4.9$$

where

$$\alpha = \frac{b(\epsilon_p + \epsilon_v)C_{.40}}{w(1 - \epsilon_p)(1 - \epsilon_v)\rho_B} \quad 4.10$$

Now x is a conversion factor which is given as

$x = (\text{Initial volume of sorbent} - \text{volume of unreacted core}) / \text{Initial volume of sorbent}$

$$= 1 - \left(\frac{r_c}{r_0} \right)^3 \quad \text{define } r_c, r_0 \quad 4.11$$

$$= 1 - (\xi)^3 \quad 4.12$$

where

$$\xi = \frac{r_c}{r_0} \quad 4.13$$

Therefore

$$\frac{\delta x}{\delta t^*} = -3(\xi)^2 \frac{\delta \xi}{\delta t^*} \quad 4.14$$

$$= -3(\xi)^2 \frac{1}{r_0} \frac{\delta r_c}{\delta t^*} \quad 4.15$$

Now the local rate of reaction at the solid surface may be expressed as follows for a reaction, first order with respect to gaseous reactant at shrinking core surface (r_c)

$$-\rho_B \frac{\delta r_c}{\delta t} = bkC_A \quad 4.16$$

Therefore

$$\frac{\delta r_c}{\delta t} = \frac{-bkC_A}{\rho_B} \quad 4.17$$

We can write

$$\frac{\delta r_c}{\delta t^*} = \frac{\delta r_c}{\delta t} \times \frac{\delta t}{\delta t^*} \quad 4.18$$

Which can be written as

$$\frac{\delta r_c}{\delta t^*} = \frac{\frac{-bkC_A}{\rho_B}}{\frac{bk \left(\frac{A_g}{F_g V_g} \right) C_{A0}}{\rho_B}} \quad 4.19$$

Initial value of the radius of grain is given as $r_0 = \frac{F_g V_g}{A_g}$ 4.20

therefore we can write

$$\frac{\delta r_c}{\delta t^*} = -r_0 \psi \quad 4.21$$

or we can write $\frac{\delta x}{\delta t^*} = 3(\xi)^2 \psi = \beta$ (say) 4.22

An approximate value of β with sufficient accuracy may be obtained from the following expression (Shon and Szekely, 1972).

$$\beta = \left[\frac{1}{F_g} (1-x)^{\frac{1}{F_g}-1} + 2\sigma^2 ((1-x)-1)^{-\frac{1}{3}} - 1 \right]^{-1} \quad 4.23$$

The above expression is based on the assumption that pore diffusion and chemical reaction are simultaneously rate limiting.

In case of active sodium carbonate it was observed that the theoretical results obtained from the model based on pore diffusion and chemical reaction being simultaneously rate limiting steps matched fairly well with the values of thermogravimetric analysis for fractional conversion, x , by Bhaskar, 1994 (See ~~appendix~~ Appendix B).

The final equation is

$$\frac{\delta \psi}{\delta y^*} + \alpha \frac{\delta \psi}{\delta t^*} + \beta = 0 \quad 4.24$$

This may be solved with initial and boundary conditions

$$\psi(0, t) = 1 = f(t^*), \psi(y^*, 0) = 0 = h(y^*) \quad 4.25$$

Assuming β as constant the above differential equation may be solved by Laplace transformation (see ~~Appendix~~ Appendix A).

To evaluate values of fractional conversion at different dimensionless time, Runge-Kutta method of fourth order was used (see ~~appendix~~ Appendix E).

5. RESULTS AND DISCUSSION

5.1 Discussion on the Model Formulated

The model formulated for the packed bed reactor assumes plug flow of gas, isothermal conditions in the bed of reactor, particles to be uniform and spherical in shape and negligible diffusive or dispersive mass transfer in the axial direction. Experimental results were taken from the literature (Bhaskar, 1994), in which fixed bed reactor was used containing 1g of active sodium carbonate dispersed in 40g of sand. An earlier study found that no sulphur dioxide removal occurred with only sand in the reactor (Jozewicz and Co-workers, 1988). It was therefore decided to use the term indicating the fractional volume of the reactive sorbent, w , present in the reactor while going for the packed bed reactor modelling. Although porosity may change with reaction time, in the present study it was assumed to be constant. The experimental data for fractional conversion, x , of active sodium carbonate with reaction time available in literature matched fairly well with combined pore diffusion and chemical reaction being rate limiting model rather than changing porosity model, see Appendix B. Therefore it was decided to keep pore diffusion and chemical reaction simultaneously rate limiting steps. Furthermore there is very little contribution by gas film diffusion for the overall rate in case of active sodium carbonate and sulphur dioxide system (Bhaskar, 1994), a constant reactant concentration in the bulk was assumed or more precisely, at the outer surface of the pellet. Which means dimensionless concentration outside the particle was assumed to be unity. In addition, for the values of reaction modulus, σ , more than 3 extent of reaction for the sorbent with respect to reaction time is nearly uniform throughout the length of the bed (Evans and Song, 1974). For active sodium carbonate and sulphur dioxide system at

tempretures 150°C , 200°C and 250°C the value of σ ranges between 3.45 to 3.67. Therefore it was decided to keep extent of reaction uniform throughout the bed.

5.2 Simulation of Breakthrough Curves Using the Formulated Model

Sulphur dioxide breakthrough curves for sulphation of active sodium carbonate dispersed in sand were simulated using the formulated packed bed reactor model. For the sulphation of active sodium carbonate breakthrough curves were obtained by plotting dimensionless exit concentration of sulphur dioxide against dimensionless time. Kinetic data obtained from the thermogravimetric experiments (Bhaskar, 1994) were used to simulate the breakthrough curves using the formulated model.

5.2.1 Model Predicted Breakthrough Curves at Different Tempretures

Breakthrough curves were simulated using the formulated model at different temprerures of 150°C , 200°C and 250°C for the sulphation of active sodium carbonate in a packed bed with inlet sulphur dioxide concentration and space velocity being 3500ppm and 900hr^{-1} respectively. It might be mentioned that rate constant, effective diffusivity and grain structures are the parameters which are affected by the temprature. With increase in temprature dimensionless length of the reactor, y^* , and reaction modulus, σ , increases. The reaction modulus, σ , can be considered as a dimensionless particle size. Particle with small values of σ might be expected to react rapidly compared with the particle of large σ due to less hinderence of reaction from intraparticle diffusion in smaller particle (Evans and Song, 1974), but the overall effect of increase in temprature is to cause more removal of sulphurdioxide in the reactor as can be seen from Figure 5.1.

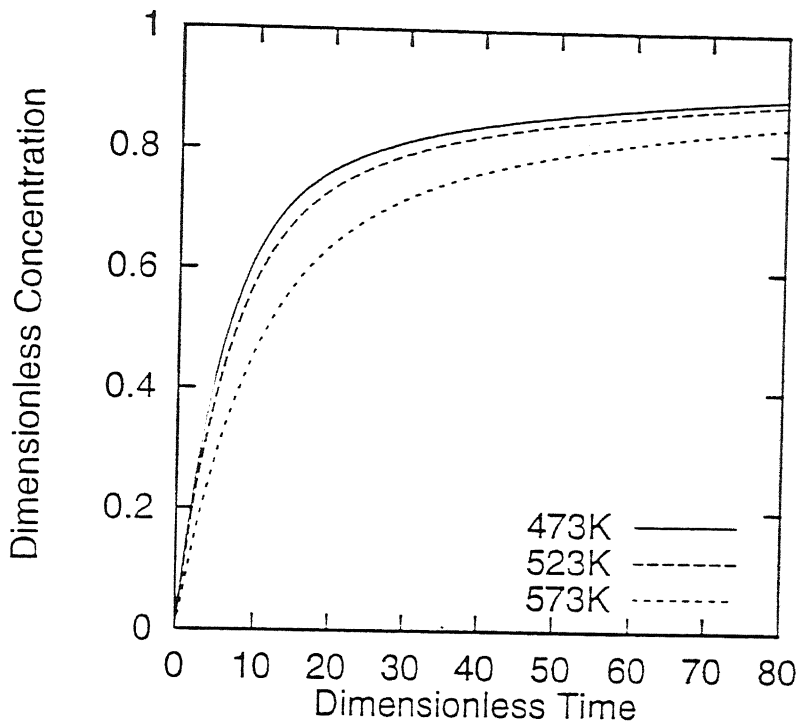


Figure 5.1: Predicted Breakthrough Curves for Sulphation of Active Sodium Carbonate at Different Temperatures with Inlet Concentration 3500ppm. *(very high)*

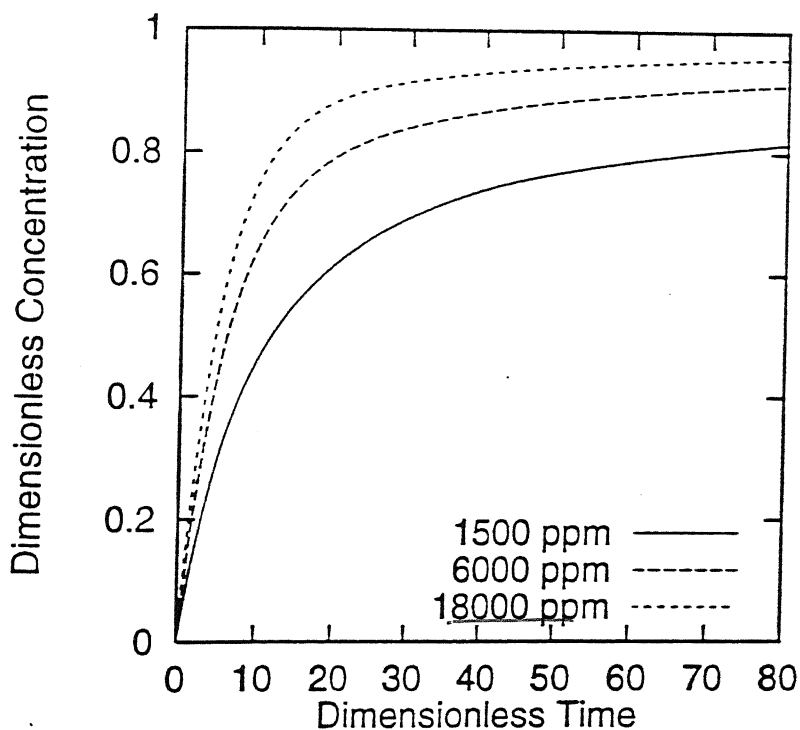


Figure 5.2: Predicted Breakthrough Curves for Sulphation of Active Sodium Carbonate at

SO₂

5.2.2 Model Predicted Breakthrough Curves at Different Concentrations

Breakthrough curves were simulated using the formulated model at different concentrations of sulphur dioxide i.e 1500, 6000 and 18000ppm for the sulphation of active sodium carbonate with temperature and space velocity being 200°C and 900hr^{-1} respectively. With the increase in the inlet concentration of sulphur dioxide, the breakthrough curve is quicker as can be seen from Figure 5.2. This is also evident from the fact that the fractional conversion of sorbent increases with increase in the inlet concentration of sulphur dioxide from 1500 to 18000ppm, indicating that with increase in partial pressure of sulphur dioxide there is higher conversion (Bhaskar, 1994). Dimensionless distance along the flow, y^* , and reaction modulus are not affected by varying the concentration at a given temperature, however, the dimensionless time, t^* , increases with the increase in concentration, hence breakthrough of sulphur dioxide will be quicker with increase in concentration.

5.3 Validation of Simulated Breakthrough Curves

Once the theoretical breakthrough curves for the sulphation of active sodium carbonate have been developed it is essential to validate them by comparing the results obtained from the model with those available in literature. Simulated breakthrough curves corroborated fairly well with the experimental results (Bhaskar, 1994) for active sodium carbonate and sulphur dioxide system. At temperature 150°C and concentration 3500ppm it was seen from the Figure 5.3 that simulated breakthrough curve matched fairly well with the experimental results. For the other two temperatures (200°C and 250°C) with same inlet sulphur dioxide concentration it can be seen from Figure 5.4 and Figure 5.5 that the experimental results are lying below the simulated curves indicating more removal in the real situation compared to the simulated one. The error between the model predicted and experimental breakthrough curves at concentration 3500ppm and temperatures 150°C , 200°C and 250°C were found out to be between 5 to 12%.

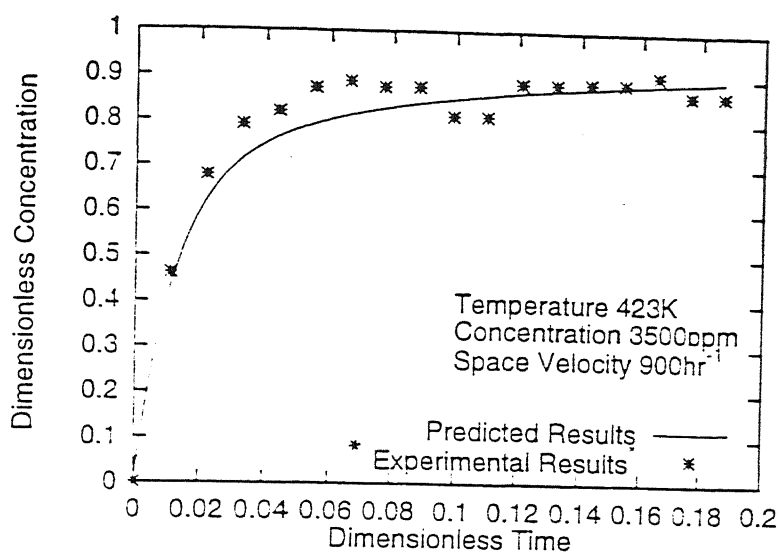


Figure 5.3: Comparison of Experimental and Simulated Breakthrough Curves for Sulphation of Active Sodium Carbonate.

* Source: Bhaskar. 1994.

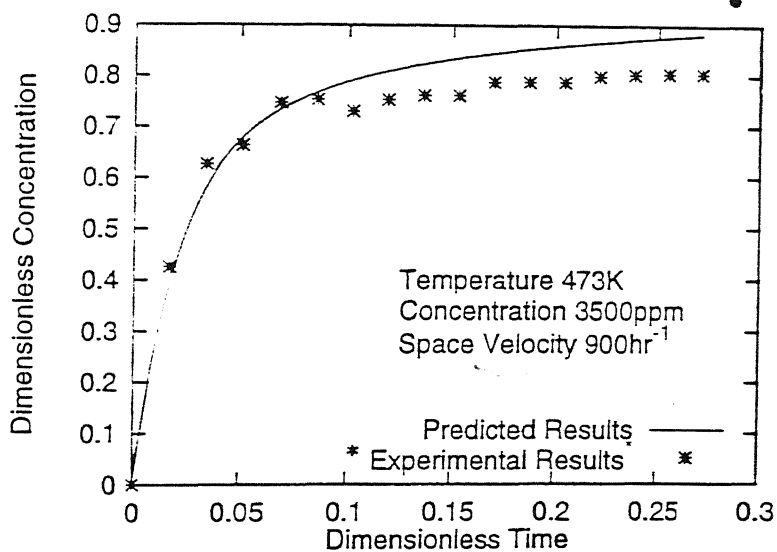


Figure 5.4: Comparison of Experimental and Simulated Breakthrough Curves for Sulphation of Active Sodium Carbonate.

* Source: Bhaskar. 1994.

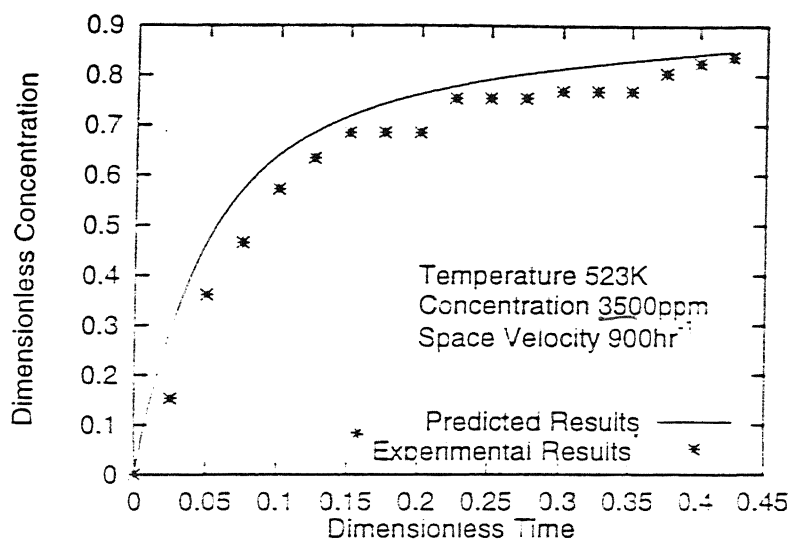


Figure 5.5: Comparison of Experimental and Simulated Breakthrough Curves for Sulphation of Active Sodium Carbonate.

* Source: Bhaskar, 1994.

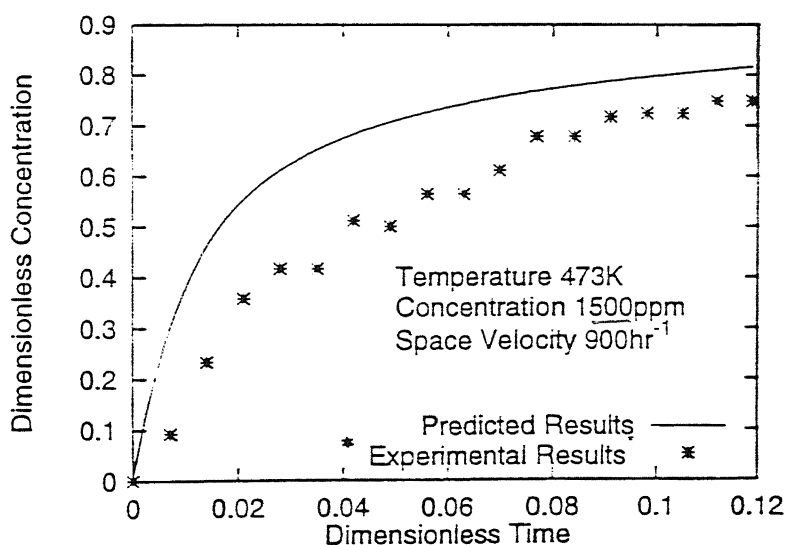


Figure 5.6: Comparison of Experimental and Simulated Breakthrough Curves for Sulphation of Active Sodium Carbonate.

* Source: Bhaskar, 1994.

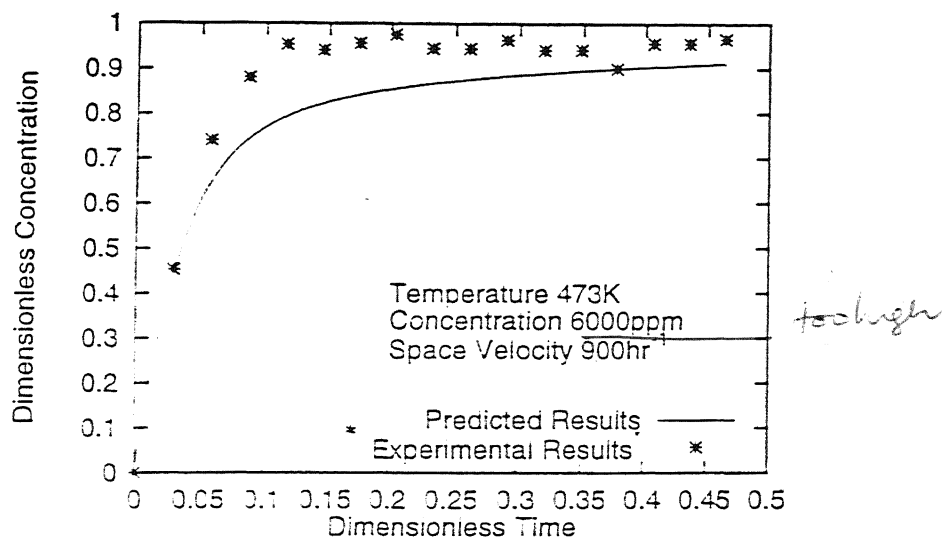


Figure 5.7: Comparison of Experimental and Simulated Breakthrough Curves for Sulphation of Active Sodium Carbonate.

* Source: Bhaskar, 1994.

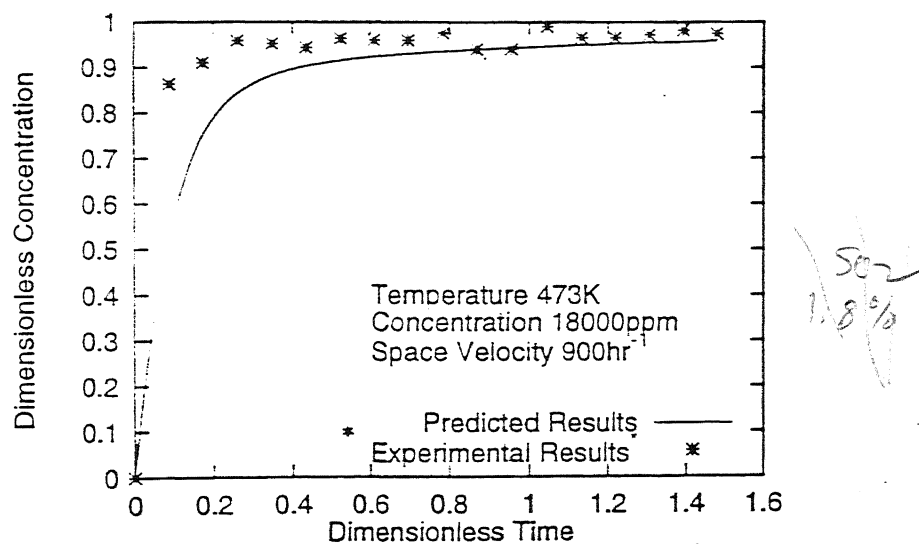


Figure 5.8: Comparison of Experimental and Simulated Breakthrough Curves for Sulphation of Active Sodium Carbonate.

* Source: Bhaskar, 1994.

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It is evident that the result of graphical integration of the area above the curve to estimate sulphur dioxide removal based on the predicted breakthrough curves are on the conservative side for the reactor design.

At concentration 1500ppm and temperature 200°C it can be from Figure 5.6 that the simulated breakthrough curve is lying above the experimentally obtained results. Although the estimate for sulphur dioxide removal is on the over conservative side but the reactor design becomes uneconomical for this case. At high concentrations of 6000ppm and 18000ppm at temperature 200°C it can be seen from the Figure 5.7 and 5.8 that experimental results and simulated breakthrough curves are close to each other.

6. CONCLUSIONS

Model predicted dimensionless outlet concentration from the packed bed reactor model using the kinetic parameters obtained from the thermogravimetric experiments performed by Bhaskar, 1994 corroborated fairly well with the actual dimensionless concentration for active sodium carbonate and sulphur dioxide system available in the literature (Bhaskar, 1994).

Breakthrough curves obtained by using the formulated model based on combined pore diffusion and chemical reaction as rate limiting steps predicted less removal of sulphur dioxide as compared to actual removal at inlet sulphur dioxide concentration of 3500ppm and temperature range between 200 and 250⁰C. It is evident that the reactor design for these situations based on the predicted curves will be on the conservative side. Infact, model data matched fairly well with the experimental data at 150⁰C.

Model predicted breakthrough curves at different concentrations and given temperature (1500, 6000 and 18000ppm at 200⁰C) were found closer to the experimental results at higher concentrations as compared to lowest concentration. It is thus evident that the reactor design based on the formulated model will be on the over conservative side at low inlet sulphurdioxide concentration.

Errors between the predicted and experimental breakthrough curves were found to be between 5 and 12%, except at low concentration when design becomes over conservative.

7. SUGGESTIONS FOR THE FUTURE WORK

A more comprehensive model taking into account the structural changes may be used to predict the conversion of sorbent with respect to time, which in turn may be incorporated in the packed bed reactor model to predict breakthrough curves with better accuracy. Also the present work did not incorporate nonisothermal conditions which may develop in the packed bed reactor. Work may be taken to model the packed bed reactor for predicting breakthrough curves under nonisothermal conditions.

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Appendix – A

Solution by Laplace Transformation

The original equation is

$$\frac{\partial v}{\partial y^*} + \alpha \frac{\partial v}{\partial t^*} + \beta = 0$$

with initial and boundary conditions as $v(0, t^*) = 1 = f(t^*)$ and $v(y^*, 0) = 0 = h(y^*)$.

Applying Laplace Transformation.

$$\mathcal{L} \left(\frac{\partial v}{\partial y^*} + \alpha \frac{\partial v}{\partial t^*} + \beta \right) = \mathcal{L}(0) \quad (1)$$

where,

$$\begin{aligned} \mathcal{L} \left(\frac{\partial v}{\partial y^*} \right) &= \frac{\partial \bar{v}(y^*, P)}{\partial y^*} \\ \mathcal{L} \left(\frac{\partial v}{\partial t^*} \right) &= P \bar{v}(y^*, S) - v(y^*, 0) \\ \mathcal{L}(\beta) &= \beta/P \end{aligned}$$

Substituting the above values in Eq. (1), we get

$$\frac{\partial \bar{v}}{\partial y^*} + \alpha P \bar{v} + \beta/P = 0$$

which can be written as

$$\frac{d\bar{v}}{(\alpha P^2 \bar{v} + \beta)} = -\frac{dy^*}{P}$$

The above equation can be further simplified as

$$\frac{1}{\alpha P^2} \ln(\alpha P^2 \bar{v} + \beta) = -\frac{1}{P} y^* + C$$

at $y^* = 0$, $\bar{v}(0, P) = 1/P$. Substituting it in Eq. (1), we get

$$\frac{1}{\alpha P^2} \ln(\alpha P + \beta) = C$$

Putting this in Eq. (1) we get

$$\frac{1}{\alpha P^2} \ln(\alpha P^2 \bar{v} + \beta) = -\frac{1}{P} y^* + \frac{1}{\alpha P^2} \ln(\alpha P + \beta)$$

which can be written as

$$\frac{1}{\alpha P^2} \ln \left\{ \frac{(\alpha P^2 \bar{\psi} + \beta)}{(\alpha P + \beta)} \right\} = -\frac{1}{P} y^*$$

or,

$$\frac{(\alpha P^2 \bar{\psi} - \beta)}{(\alpha P + \beta)} = e^{-\alpha P y^*}$$

Therefore,

$$\begin{aligned} \bar{\psi} &= \frac{\{(\alpha P + \beta)e^{-\alpha P y^*} - \beta\}}{\alpha P^2} \\ &= \frac{e^{-\alpha P y^*}}{P} - \frac{\beta}{\alpha} \left\{ \frac{e^{-\alpha P y^*}}{P^2} \right\} - \frac{\beta}{\alpha P^2} \end{aligned}$$

To determine the value of ψ , we apply inverse Laplace Transformation on the above equation. Therefore

$$\begin{aligned} \psi &= \mathcal{L}^{-1}(\bar{\psi}) \\ &= \mathcal{U}_{\alpha y^*}(t^*) + \frac{\beta}{\alpha} (t^* - \alpha y^*) \mathcal{U}_{\alpha y^*}(t^*) - \frac{\beta}{\alpha} t^* \end{aligned}$$

or,

$$\psi = \left(1 - \frac{\beta t^*}{\alpha} - \beta y^* \right) \mathcal{U}_{\alpha y^*}(t^*) - \frac{\beta}{\alpha} t^*$$

where, $\mathcal{U}_{\alpha y^*}(t^*)$ is a unity function as is given as

$$\mathcal{U}_{\alpha y^*}(t^*) = \begin{cases} 0 & \text{if } t^* < \alpha y^* \\ 1 & \text{if } t^* > \alpha y^* \end{cases}$$

Appendix B

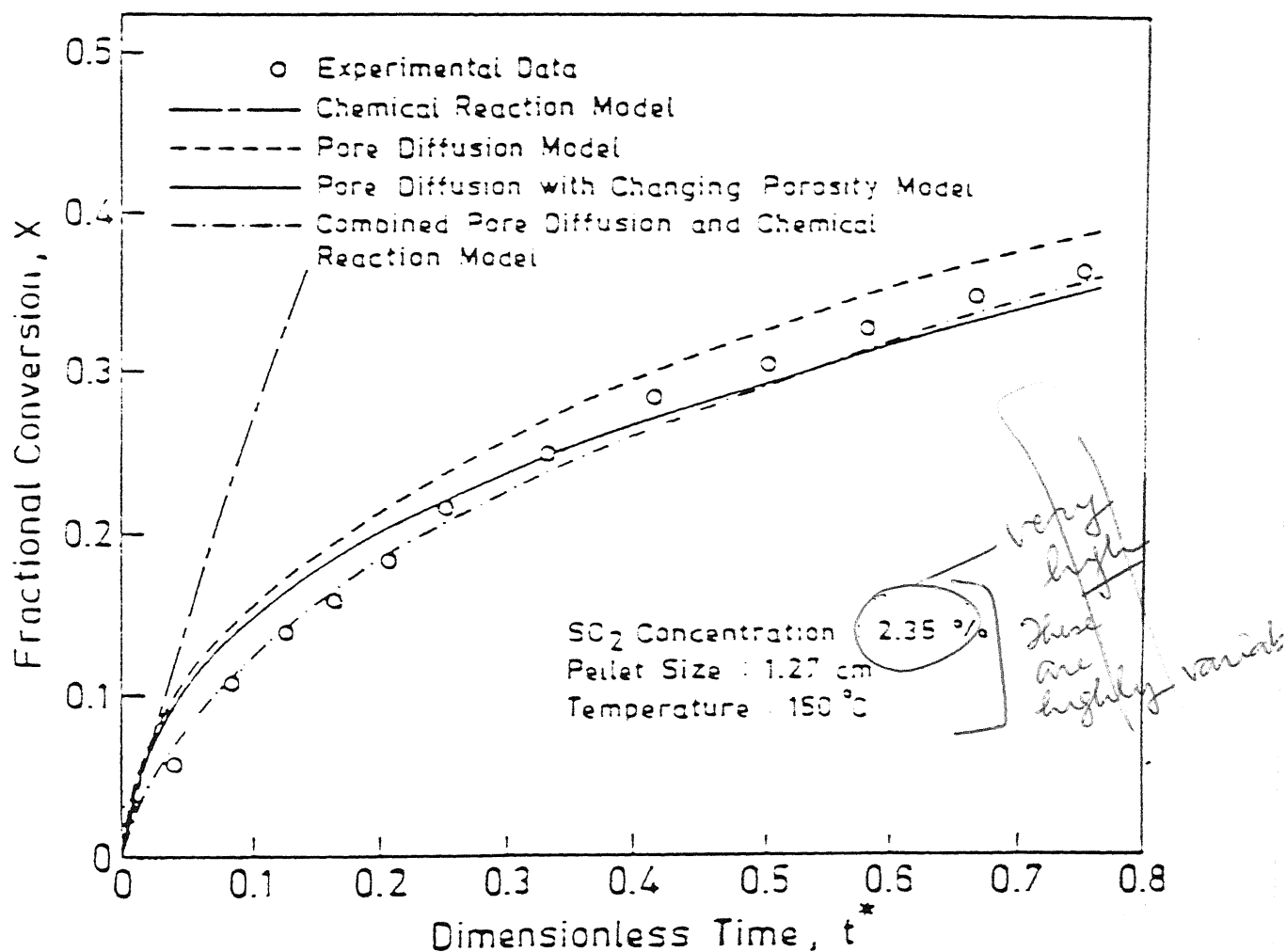


Figure B.1: Predicted Conversion and Experimental Data for Sulphation of Active Sodium Carbonate.

*Source: Bhaskar, 1994.

Appendix C

*DATA USED FOR THE PREDICTION OF BREAKTHROUGH CURVES FOR SULPHATION OF ACTIVE SODIUM CARBONATE.

(*Source: Bhaskar, 1994).

Length of the packed bed (y) = 39.1cm.

Radius of particle (R_0) = 0.635cm.

Molar density of the solid reactant (ρ_B) = 0.0239g-mole/cm³.

Grain shape factor (F_g) = 3.

Particle shape factor (F_p) = 3.

Porosity of the bed (ϵ_p) = 0.42

Superficial velocity (U) = 4cm/sec

Fractional volume of reactive solids (w) = 1/40

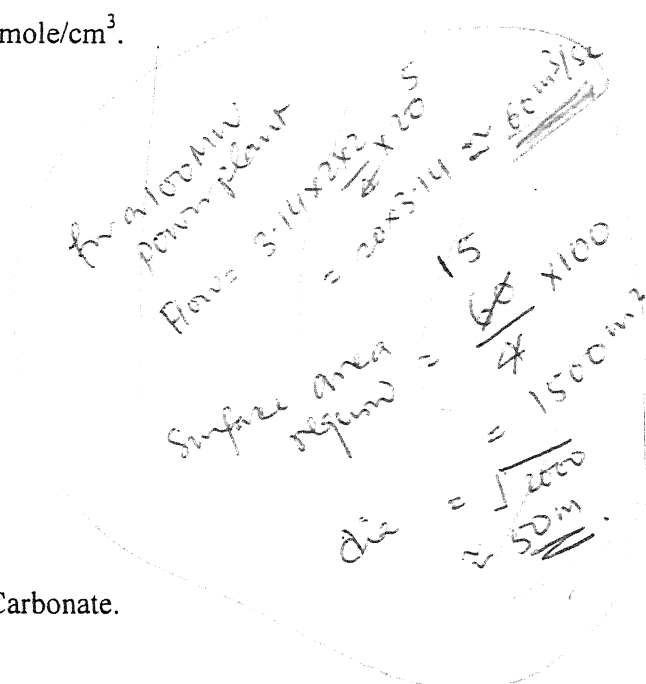


Table C.1: Physical Parameters of Active Sodium Carbonate.

<u>Temperature</u> °C	<u>Pore Volume</u> cm ³ /gm	<u>Porosity</u>	<u>BET Surface Area</u> m ² /gm
150	0.49	0.55	3.14
200	0.47	0.54	2.70
250	0.45	0.53	2.50

Table C.2: Values of Rate Constant (k) and Effective Diffusivity (D_e) for Sulphation of Active Sodium Carbonate.

<u>Tempreture</u> °C	<u>Rate Constant</u> k	<u>Effective Diffusivity</u> D_e
150	1.48×10^{-4}	0.0084
200	2.25×10^{-4}	0.0111
250	3.91×10^{-4}	0.0170

Appendix D

Table D.1: Experimental and Predicted Values of Breakthrough Curves for Sulphation of Active Sodium Carbonate at 150⁰C with Inlet Sulphurdioxide Concentration of 3500ppm.

<u>Dimensionless Time</u>	<u>Dimensionless Outlet Concentration</u>	
	<u>Experimental*</u>	<u>Predicted</u>
0.000	0.000	0.000
0.011	0.462	0.627
0.022	0.678	0.709
0.033	0.791	0.754
0.044	0.820	0.783
0.057	0.873	0.804
0.067	0.888	0.821
0.083	0.876	0.844
0.100	0.812	0.853
0.117	0.885	0.865
0.150	0.885	0.883
0.167	0.888	0.887
0.184	0.906	0.895
0.200	0.864	0.901

*Source: Bhaskar, 1994.

Table D.2: Experimental and Predicted Values Breakthrough Curves for Sulphation of Active Sodium Carbonate at 200⁰C and Inlet Sulphurdioxide Concentration of 3500ppm.

<u>Dimensionless Time</u>	<u>Dimensionless Outlet Concentration</u>	
	<u>Experimental</u> ⁻	<u>predicted</u>
0.000	0.000	0.000
0.017	0.426	0.528
0.034	0.626	0.665
0.051	0.683	0.721
0.068	0.747	0.757
0.085	0.753	0.782
0.102	0.730	0.801
0.127	0.753	0.823
0.153	0.761	0.838
0.178	0.822	0.852
0.208	0.788	0.861
0.229	0.788	0.870
0.255	0.805	0.877
0.280	0.813	0.886

*Source: Bhaskar, 1994.

Table D.3: Experimental and Predicted Values Breakthrough Curves for Sulphation of Active Sodium Carbonate at 250⁰C and Inlet Sulphurdioxide Concentration of 3500ppm.

<u>Dimensionless Time</u>	<u>Dimensionless Outlet Concentration</u>	
	<u>Experimental*</u>	<u>Predicted</u>
0.000	0.000	0.000
0.025	0.153	0.376
0.051	0.361	0.541
0.076	0.465	0.620
0.101	0.572	0.670
0.126	0.634	0.706
0.152	0.685	0.732
0.189	0.712	0.761
0.227	0.685	0.784
0.265	0.715	0.800
0.303	0.754	0.815
0.341	0.768	0.827
0.379	0.805	0.837
0.417	0.826	0.848

*Source: Bhaskar, 1994.

Table D.4: Experimental and Predicted Values of Breakthrough Curves for Sulphation of Active Sodium Carbonate with Inlet Sulphurdioxide Concentration of 1500ppm and tempreture 200⁰C.

<u>Dimensionless time</u>	<u>Dimensionless Outlet Concentration</u>	
	<u>Experimental*</u>	<u>Predicted</u>
0.000	0.000	0.000
0.014	0.233	0.525
0.021	0.358	0.591
0.028	0.417	0.636
0.035	0.417	0.669
0.042	0.512	0.695
0.055	0.501	0.733
0.065	0.565	0.747
0.076	0.611	0.771
0.087	0.678	0.780
0.098	0.717	0.797
0.110	0.717	0.810
0.120	0.724	0.816
0.131	0.748	0.824

* Source bhaskar, 1994.

Table D.5: Experimental and Predicted Values of Breakthrough Curves for Sulphation of Active Sodium Carbonate with Inlet Sulphurdioxide Concentration of 6000ppm and Temperature 200°C.

<u>Dimensionless Time</u>	<u>Dimensionless Outlet Concentration</u>	
	<u>Experimental*</u>	<u>Predicted</u>
0.000	0.000	0.000
0.029	0.453	0.645
0.058	0.740	0.738
0.087	0.880	0.785
0.116	0.953	0.814
0.145	0.941	0.834
0.174	0.956	0.849
0.218	0.976	0.866
0.262	0.945	0.879
0.305	0.964	0.889
0.349	0.942	0.897
0.393	0.969	0.903
0.436	0.901	0.909
0.480	0.957	0.914
0.523	0.961	0.918

* Source: Bhaskar, 1994.

Table D.6: Experimental and Predicted Values of Breakthrough Curves for Sulphation of Active Sodium Carbonate with Inlet Sulphurdioxide Concentration of 18000ppm and temperture 250°C.

<u>Dimensionless Time</u>	<u>Dimensionless Outlet Concentration</u>	
	<u>Experimental*</u>	<u>Predicted</u>
0.000	0.000	0.000
0.087	0.863	0.803
0.174	0.910	0.857
0.261	0.958	0.882
0.348	0.952	0.899
0.435	0.943	0.911
0.522	0.964	0.920
0.654	0.960	0.929
0.783	0.976	0.937
0.915	0.940	0.945
1.044	0.990	0.953
1.178	0.965	0.961
1.305	0.971	0.971
1.570	0.982	0.979

*Source: Bhaskar.1994.

Appendix E

SOLUTION FOR THE FRACTIONAL CONVERSION, USING RUNGE- KUTTE METHOD

```
implicit real (a-z,o-z)
print*, 'specify sigma,h,tmax'
read*,sigma,h,tmax
open(unit=21,file=concen.out')
ti=0.0
x=0.0
n=int(tmax/h)
write(21,24)sigma
24  format(5x,'the value of sigma =',2x,f6.3/)
write(21,24)
25  format(8x,'time t*',7x,'beta',9x,'x(t*)',/)
xi=0.0
bit=beta(xi,sigma)
t=0.0
write(21,22)y,bit,xi
do i=2,n
xi=x
rk0=h*beta(xi,sigma)
rk1=h*beta(xi+0.5*rk0,sigma)
rk2=h*beta(xi+0.5*rk1,sigma)
rk3=h*beta(xi+rk2,sigma)
x=xi+(rk0+2.0*rk1+2.0*rk2+rk3)/6.0
b=beta(x,sigma)
bit=b
t=h*(i-1)
if(x.ge.0.999) goto 90
write(21,22)t,bit,x
22  format(5x,4(f10.6,3x))
100 end do
90  write(21,22)t,bit,x
stop
end
function beta(x,sigma)
implicit real(a-h,o-z)
exp=-1/3
expo2=-2/3
f1=2.0*sigma*sigma*((1.0-x)**expo1-1.0)
f2=((1.0-x)**expo2)/3.0
beta=1.0/(f1+f2)
return
end
```